REACTIONS OF ALDEHYDES WITH AMINES I
A NEW ALDEHYDE REAGENT

By

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INTRODUCTION

Preliminary attempts to condense N,N-dibenzyl-m-phenylenediamine with aromatic aldehydes to form substituted tetraamino-triphenylmethanes were unsuccessful. However, during these attempts it was observed that the addition of an aldehyde to an alcoholic solution of the diamine containing a small amount of mineral acid caused the immediate formation of an intense red color which was followed by a striking green fluorescence at various time intervals depending upon the type of aldehyde used. It was apparent that if this reaction could be shown to be specific it would be an excellent test for aldehydes. Part I of this dissertation deals with the development of this test. Part II is concerned with the preparation of the substituted tetraamino-triphenylmethanes mentioned above. Attempts to prepare these compounds from the free amine led instead to Schiff bases. However, use of the acetylated or benzoylated derivative of the amine resulted in the formation of the desired compounds in good yields.

PART I

A NEW REAGENT FOR THE DETECTION OF ALDEHYDES

Discussion of Other Reagents

There are several reagents in use at the present time for the detection of aldehydes. The use of some of these, including Tollen's reagent (ammoniacal silver nitrate) and Fehling's solution, depends upon the fact that most aldehydes are easily oxidized and hence show a characteristic reducing action. Thus the complex silver ions in Tollen's reagent are reduced to metallic silver and the aldehyde is oxidized to the corresponding acid. Fehling's solution is not used as a general test for aldehydes since it oxidizes only those members which belong to the aliphatic series. However, this property is a very useful one and Fehling's solution is used extensively in distinguishing between the two classes of aldehydes.

These tests which are based upon the reducing properties of aldehydes are not specific since other reducing agents give the same reactions. Some of the compounds which interfere are hydrazines, hydroxylamines, and alpha-hydroxy carbonyl compounds such as hydroxyacetone, benzoin and monosaccharic acid. The reducing properties of this latter class of compounds may be explained by the fact that there is probably an equilibrium between the ordinary hydroxyacetone form and the ene-diol

$$CH_3.CO.CH_2OH \rightleftharpoons CH_3.C(OH):CHOH$$

which is oxidized much more easily.

Probably the most generally used test for aldehydes is that of Schiff[1] who observed that fuchsin solutions lose their color on treatment with sodium sulfite or sulfur dioxide and that the color is regenerated on addition of an aldehyde. Attempts to explain this phenomenon have been widely divergent in nature and the problem was not solved until Wieland and Scheuing[2] did their work in 1921. They showed that the decolorization of fuchsin is due to the addition of the sulfurous acid to the ends of the quinonoid system, forming tri-p-amino-triphenylmethane-sulfonic acid which then adds a second molecule of sulfurous acid to form the colorless aminosulfinic acid

When an aldehyde is added to a solution of this compound it condenses with the sulfinic acid group in much the same way that aldehydes react with alkali bisulfites. This new compound is now free to condense another of its amine groups with sulfurous acid and the newly formed amino-sulfinic acid group can, in its turn, add another molecule of aldehyde. The new compound is unstable and loses sulfurous acid, regenerating the quinonoid system, the structure of the violet dye, upon whose formation the test depends, is as follows:

the acceptance of this theory makes it necessary to discard two theories which have been very popular and which still find a place in some of the latest and best books on organic chemistry. The first[5] is based on the assumption that the sulfite reduces the dye to the leuco base and that, subsequently, the aldehyde reoxidizes it to the color base. Spectral absorption studies have shown that the new color is not the same as that of the original fuchsin and an investigation[6] in this laboratory has shown that aldehydes do not oxidize the leuco bases of polyaminotriphenylmethanes to the color bases. In spite of the objections to this theory, it is the one most generally held by organic chemists today. The second theory[7] assumes that the sulfurous acid adds to the ends of the quinonoid system, rendering it colorless, and that the addition of an aldehyde causes the transfer of the sulfurous acid to the latter with the regeneration of the color of the dye. This explanation, although it has more merit than the one described above, is also shown to be invalid by the work of Wieland and Scheuing[8].

As was mentioned above, Schiff's reagent is undoubtedly the most widely used of all the aldehyde reagents and it has been an invaluable tool in the study of the aldehydes and the sugars. However,

it the certain disadvantages. The reagent when made up correctly and when fresh is very sensitive; however, when allowed to stand in the laboratory it loses this sensitivity rapidly. The specificity of this reagent also leaves something to be desired. In the first place, it gives a positive test slowly with acetone, methanol and ethanol as well as with certain other non-aldehyde oxygenated substances. On the other hand, para-substituted aromatic aldehydes such as p-aminobenzaldehyde, p-dimethylaminobenzaldehyde, p-hydroxybenzaldehyde, anisaldehyde, veratric aldehyde, vanillin and piperonal give poor reactions or none at all. Heptaldehyde and other higher aliphatic aldehydes give very poor reactions.

Besides the three important tests described above, there are several others which are worthy of brief mention in this summary.

Penzoldt and E. Fischer[5] describe a test which makes use of diazobenzenesulfonic acid dissolved in water containing sodium hydroxide and sodium amalgam. Addition of an aldehyde causes the appearance of a red color in from ten to twenty minutes. This red color is the same for all aldehydes. Benzaldehyde can be detected in 1/3000 dilution and it is claimed that the reaction is more specific than the Schiff test, although acetone and acetoacetic ester give positive tests and chloral does not react. The mechanism of the reaction is not known.

Angeli and Rimini[7] have developed a test for aldehydes which is based on the condensation of aldehydes with the nitroxyl group to form hydroxamic acids which yield highly colored complex iron salts with the ferric ion. A mixture of the test solution and a little benzenesulfohydroxamic acid is treated with alkali. This breaks up the latter compound into benzenesulfinic acid and the nitroxyl radical

$$C_6H_5 \cdot \underset{OH}{\overset{O}{S}} : NOH \longrightarrow C_6H_5 \cdot SO_2H \ + \ NOH$$

which then condenses with the aldehyde if there is one present

$$RCHO \ + \ NOH \longrightarrow RCH(OH).NO \longrightarrow R \cdot \underset{OH}{C} : NOH$$

to form the corresponding hydroxamic acid. If ferric ammonium sulfate is added to the acidified solution the intense red color of the iron complex signifies the presence of aldehyde. This reaction is used usually as a spot test. The same p-substituted aromatic aldehydes which do not react with Schiff's reagent fail also to react here.

The object of Part I of this dissertation is to describe the preparation, properties and reactions of N,N-dibenzyl-m-phenylenediamine. This substance has properties which, it is believed, make it a more useful general reagent for aldehydes than any previously devised.

The Synthesis of N,N-Dibenzyl-m-phenylenediamine

This compound was prepared by Desai[8], who was unable to purify it and reported it as a viscous oil which oxidized readily in the air. It was also prepared as an intermediate by Bayer & Co.[9] in their synthesis of N,N-dibenzyl-N'-acetyl-m-phenylenediamine. However, in this case the acetyl derivative was prepared directly from the reaction mixture obtained in the reduction of dibenzyl-m-nitraniline and no attempt was made to purify the free amine.

After a series of preliminary experiments, a method has been developed in this laboratory for the preparation and isolation of this compound in pure crystalline form. As such, it is stable enough to be kept for months if ordinary precautions are taken to guard it against oxidation. Like most similar compounds, it is more stable when in a high state of purity. The method used is similar in general to that used by Desai, but it differs from Desai's procedure in several important points. Dibenzyl-m-nitraniline is prepared by benzylating m-nitraniline with benzyl chloride and anhydrous sodium acetate in the presence of a small amount of iodine as a catalyst. The resulting nitro compound is reduced to the diamine with zinc and hydrochloric acid.

<u>Starting materials</u>. Since the purity of the materials used in this reaction is of more importance than usual, procedures for the purification of m-nitraniline and benzyl chloride will be given. It was found that if care were observed in purifying these substances the

purification of the dibenzyl-m-phenylenediamine was greatly simplified. In fact, it was almost impossible to purify the product obtained from incompletely purified starting materials. In the series of reactions under consideration the products became increasingly difficult to purify as one passes from step to step and a high degree of purity is essential in the starting materials.

The m-nitroaniline used was Eastman's technical grade which was freed from tarry impurities by distillation at 8 mm. Under these conditions there was no decomposition and the distillate, after solidification, melted sharply at 112°C. and was perfectly satisfactory for use in the reaction. It was found that distillation was faster, more economical and gave a better product than crystallization from water or from dilute alcohol.

The benzyl chloride used was Eastman's best grade. The small amount of hydrochloric acid in this was removed by shaking first with 5% sodium carbonate solution and then with water. The acid-free product was dried over calcium chloride and then distilled under reduced pressure. At 10 mm. the boiling range was 61-63°C. The benzyl chloride must not be distilled at ordinary pressure because slight decomposition ensues.

<u>The Preparation of N,N-Dibenzyl-m-nitraniline.</u> In a 1 liter round-bottomed flask were placed 138 grams (1 mole) of purified m-nitraniline, 253 grams (2 moles) of benzyl chloride, 164 grams (2 moles) of powdered anhydrous sodium acetate and 1.5 grams of iodine. The flask was placed in an oil bath under a hood and the temperature of the bath raised slowly (one hour) to 115-120°C., where it was maintained for a minimum of seven hours. During this time the viscous oil was stirred efficiently with an air-driven stirrer—not a motor-driven stirrer because of the corrosive action of benzyl chloride vapors. The temperature of the bath should be maintained within the designated limits during the reaction. Above 120°C., appreciable quantities of decomposition products are formed, while below 115°C., there is danger of incomplete benzylation with subsequent difficulty in separating the mono- from the dibenzylated product.

When the reaction was completed, the resulting black oil was poured into a beaker containing two liters of water and stirred rapidly in order to dissolve any excess sodium acetate. During this stirring the oil became more and more viscous and finally solidified to a brown mass. The water was decanted and the mass washed several times with water. Then 500 cc. of 95% alcohol was added and the product was allowed to remain in contact with this overnight. Filtration at the pump left the compound in the form of bright yellow crystals which were washed more with alcohol and then recrystallized from about three liters of alcohol.

An excess of alcohol must be used to prevent the solution from reaching the saturation point at a temperature above the melting point of the compound (72°C.)

If the product, which consists of bright yellow leaflets, melts at 71°C. or above, a second recrystallization is unnecessary. Although Dessi reports the melting point as 75-76°C., elaborate efforts in this laboratory have failed to raise the melting point above 72°C. The substance sometimes shows dimorphic properties. In these cases it melts first at 72°C., resolidifies on continued slow heating and melts again at 78°C. If the temperature is raised slowly from room temperature, with the capillary in the bath, the lower melting point is not observed. A Maquenne block has been very useful in studying this melting point and several others of a similar nature which were encountered in the triphenylmethane series.

A second batch of crystals was recovered from the mother liquor and recrystallized. The total yield averaged about 180 grams or 68% of theory.

The Reduction of Dibenzyl-m-nitraniline. In a 5 liter flask was placed 100 grams of dibenzyl-m-nitraniline. This was dissolved in a mixture of 800 cc. of 95% alcohol and 800 cc. of concentrated hydrochloric acid, forming an almost colorless solution (the hydrochloride is colorless). To this solution granulated zinc was added just fast enough to maintain a vigorous evolution of hydrogen. About 200-250 grams of zinc was required and after the addition of most of this quantity frequent tests were made to determine whether the reduction was complete. This test is based upon the fact that the hydrochloride of the nitro compound is white but is easily hydrolyzed, on contact with water, to the yellow free base. Therefore, as long as any of the nitro compound remains unreduced, a yellow color is produced when a few drops of the reaction mixture is poured into water. When this test was negative the solution was filtered to remove unreacted zinc and placed in the ice-box. On standing overnight, the hydrochloride of N,N-dibenzyl-m-phenylenediamine separated out as a solid mass of beautiful white crystals. These were filtered at the pump and the mother liquor pressed out as completely as possible. The white solid was placed in a 2 liter beaker and stirred thoroughly with 1800 cc. of water in order to liberate the free amine. This separated in the form of a bulky, flocculent, white precipitate which was filtered, washed several times with water, and then stirred again with 1800 cc. of water in order

to remove as much as possible of the remaining HCl and $ZnCl_2$. Again the amine was separated by filtration, washed with water, and finally suspended in 1 liter of 8% sodium hydroxide solution and allowed to remain overnight in the refrigerator in order to remove all traces of acid and zinc chloride. The substance also assumed a much better crystalline form on standing in this solution. The slightly yellow crystals were filtered off and washed several times with water and then dried in a vacuum desiccator over solid potassium hydroxide. The yield of crude dry product from three similar preparations averaged 75 grams or 90% of theory. Recrystallization from 500 cc. of alcohol gave 65 grams of the substance in the form of well-defined white crystals which melted sharply at 101°C. After drying in an Abderhalden apparatus at 80°C. over sulfuric acid at 10 mm., nitrogen analysis (Kjeldahl) showed 8.78% and 8.78%; nitrogen analysis (Dumas) showed 8.67% N. Calculated: 8.78% N.

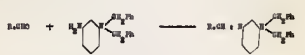
The Properties of N,N-Dibenzyl-m-phenylenediamine

Empirical formula	$C_{20}H_{20}N_2$
Structural formula	

Crystalline form and color	White crystals	
Molecular weight	288.38	
Melting point	101°C.	
Yield	80%	
Analyses	Found	Calculated
Nitrogen	9.72%	9.72%
	9.75	
	9.67	
Solubilities		
Water	Insoluble	
Alcohol	Slightly soluble cold	
Acetone	Soluble	
Benzene	Soluble	
Concentrated HCl	Difficultly soluble cold	

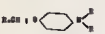
Theory

In the introduction it was stated that N,N-dibenzyl-m-phenylenediamine reacts with aldehydes in the presence of mineral acids with the formation of intense colors and a characteristic green fluorescence. Further study showed that when the amine and an aromatic aldehyde were heated together in neutral alcohol solution the Schiff base separated as a yellow oil

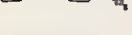


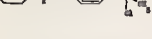
These condensation products do not crystallize from any of the solvents tried, but may be obtained, by repeated extraction with alcohol, as amorphous yellow powders which are pure enough for analysis. When these compounds are dissolved in anhydrous ether and subjected to treatment with dry HCl gas, blood-red resins separate from the solutions. This accounts for the intense color mentioned above. If however, the HCl treatment is continued, the red color gradually fades to light yellow. The light yellow compounds slowly return to the red form if left in the air. If they are treated with water, the change to red is followed by a slow loss of color and the appearance of the odor of the aldehyde, indicating hydrolysis to the original amine and aldehyde. All of these facts indicate that the Schiff bases under consideration form bright red monohydrochlorides and light yellow dihydrochlorides, the latter being unstable in the presence of moisture.

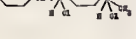
A search of the literature was made to see if similar observations had been made previously in regard to analogous compounds and it was found that Moore and Gale[10] had noticed that Schiff bases in which one portion of the molecule consisted of an N,N-dimethyl-phenylenediamine residue showed the same properties exactly as those described above. From their study they concluded that bases of the formula



form darker mono- salts and lighter di- salts than the bases themselves. They suggested three possible formulas for the red monohydrochloride. Two of these differed only in the nitrogen selected for the addition of the first HCl molecule. The third formula assumes a paraquinoid structure (3) for the monohydrochloride which is changed back to the benzenoid structure on addition of the second molecule of HCl.

(1) 

(2) 

(3) 

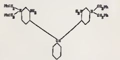
In a second paper[11], Moore sought to establish this last theory by preparing the corresponding m-dimethylamino derivatives, which could not possibly assume quinonoid structures. If these compounds did not form highly colored monohydrochlorides the evidence would be overwhelmingly in favor of the quinonoid theory. Moore reports that these compounds actually do not show marked color changes on treatment with HCl. However, he states that no definite conclusions could be drawn because of the physical properties of these bases. In contradistinction to the crystalline properties of the para compounds, the meta derivatives were uncrystallizable resins, which molecular weight determinations showed to be low molecular weight polymers.

Since it seemed strange that these compounds, whose physical properties coincided perfectly with those of the corresponding m-dibenzylamino derivatives prepared in this laboratory, did not also form highly colored monohydrochlorides, the work of Moore was repeated. In opposition to Moore's results, experiments in this laboratory show conclusively that the m-dimethylamino derivatives, when subjected to treatment with dry HCl, form highly colored monohydrochlorides and almost colorless dihydrochlorides just as do the p-dimethylamino and m-dibenzylamino derivatives. This is considered proof that the quinonoid theory is invalid.

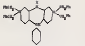
Every explanation offered thus far for these color reactions has as many disadvantages as advantages. However, there was many color phenomena which do not lend themselves easily to explanation. Several

anomalies have been encountered in the present investigation. For example, it seems difficult to account for the bright red color of dimethyl-m-nitraniline in view of the fact that the para isomer is pale yellow in color. Also dibenzyl-m-nitraniline, which theoretically should be darker than the dimethyl-m-nitraniline, is bright yellow.

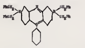
Hence, the formation of the monohydrochlorides of the Schiff bases offers a feasible explanation of the color reactions. However, since these compounds are not fluorescent, this latter characteristic of the test must be accounted for by a secondary reaction. Although repeated efforts to isolate another pure compound have failed, there is little doubt about the origin of the fluorescence. It will be remembered that this test was discovered during an apparently vain attempt to split out water from two molecules of the m-diamine and one molecule of aldehyde to form substituted tetraamino-triphenylmethanes



the appearance of the fluorescence can be accounted for by assuming that this reaction does take place to a certain extent and that ammonia splits out to form the substituted dihydroacridine



and that this oxidizes spontaneously to the fluorescent acridine derivative



This theory is well substantiated by the following facts:

(1) Some of these acridine derivatives were prepared from the acetylated reagent and they exhibit a characteristic fluorescence which is indistinguishable from that observed in the test.

(2) A study in this laboratory of the reactions of aldehydes with aromatic diamines showed that, while color reactions are noted in all cases, only the m-diamines give fluorescent products. These are, of course, the only amines capable of reacting with aldehydes to form

acridines. Compounds such as m-phenylenediamine, m-toluylenediamine, and N,N-dimethyl-m-phenylenediamine were found to give reactions similar to those given by the dibenzyl derivative. However, in these cases the fluorescence was much weaker and was slower in appearing.

(8) It seemed strange at first that ammonia could be split out of the triphenylmethane derivatives at room temperature; however, attempts to deacetylate compounds such as 2,2'-diacetamino-4,4'-bis-dibenzylamino-triphenylmethane

led directly to the acridine derivatives, indicating that the free tetramino-triphenylmethanes are more easily cyclized than is usual in this series. The heavy dibenzylamine groups are undoubtedly responsible for this.

Schiff Bases from N,N-dibenzyl-m-phenylenediamine

These compounds were prepared by adding the aldehydes slowly to equivalent amounts of the amine dissolved in boiling alcohol. In most cases continuation of the heating resulted in the separation of the product as a yellow or light orange oil within ten minutes. However, the products from anisaldehyde and o-methoxybenzaldehyde separated only on cooling. Repeated efforts to recrystallize these substances were unsuccessful. They separated always as oils which became amorphous resins after standing in the refrigerator. These non-crystalline compounds, however, were prepared in form pure enough for analysis by repeated extraction with hot alcohol followed by separation from a mixture of equal parts of alcohol and dioxane. They were powdered and then dried carefully over sulfuric acid in a vacuum desiccator at 10 mm. All of these compounds melted over wide ranges below 100°C. They form intensely colored monohydrochlorides and almost colorless dihydrochlorides.

Benzylidene-p-dibenzylaminoaniline

Empirical formula	$C_{27}H_{24}N_2$
Structural formula	

Crystalline form and color	Light yellow amorphous solid
Molecular weight	376.21
Melting point	None
Yield	70%
Analyses	Found Calculated
Nitrogen	7.48% 7.44%
Solubilities	
Water	Insoluble
Alcohol	Slightly soluble hot
Acetone	Very soluble
Ether	Soluble
Benzene	Soluble
Dioxan	Soluble

Salicylidene-m-dibenzylaminoaniline

Empirical formula $C_{27}H_{24}N_2O$

Structural formula

Crystalline form and color	Light orange amorphous solid
Molecular weight	388.21
Melting point	None
Yield	68%
Analyses	Found Calculated
Nitrogen	7.16% 7.17%
Solubilities	
Water	Insoluble
Alcohol	Slightly soluble hot
Acetone	Very soluble
Ether	Soluble
Benzene	Soluble
Dioxan	Soluble

Cinnamylidene-p-dibenzylaminoaniline

Empirical formula	$C_{29}H_{26}N_2$
Structural formula	

Crystalline form and color	Light orange amorphous solid	
Molecular weight	402.19	
Melting point	None	
Yield	62%	
Analyses	Found	Calculated
Nitrogen	6.77%	6.97%
Solubilities		
Water	Insoluble	
Alcohol	Slightly soluble hot	
Acetone	Very soluble	
Ether	Soluble	
Benzene	Soluble	
Dioxane	Soluble	

p-Chlorobenzylidene-m-dibenzylamino-aniline

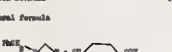
Empirical formula	$C_{27}H_{23}N_2Cl$
Structural formula	

Crystalline form and color	Light yellow amorphous solid	
Molecular weight	410.96	
Melting point	None	
Yield	87%	
Analyses	Found	Calculated
Nitrogen	6.62%	6.82%
Solubilities		
Water	Insoluble	
Alcohol	Slightly soluble hot	
Acetone	Soluble	
Benzene	Soluble	
Ether	Soluble	
Dioxane	Soluble	

Anisylidene-m-dibenzylaminoaniline

Empirical formula $C_{28}H_{26}N_2O$

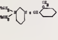
Structural formula



Crystalline form and color	Pale yellow amorphous solid
Molecular weight	406.52
Melting point	None
Yield	80%
Analyses	Found Calculated
Nitrogen	6.7?% 6.90%
Solubilities	
Water	Insoluble
Alcohol	Soluble hot
Acetone	Very soluble
Ether	Soluble
Benzene	Soluble
Dioxane	Soluble

o-Methoxybenzylidene-p-dibenzylaminoaniline

Empirical formula	$C_{28}H_{26}N_2O$
Structural formula	



Crystalline form and color	Pale yellow amorphous solid	
Molecular weight	406.52	
Melting point	None	
Yield	60%	
Analyses	Found	Calculated
Nitrogen	6.92%	6.89%
Solubilities		
Water	Insoluble	
Alcohol	Soluble hot	
Acetone	Very soluble	
Ether	Soluble	
Benzene	Soluble	
Dioxan	Soluble	

Description of the Test for Aldehydes

The stock solution consists of a 1% solution of N,N-dibenzyl-m-phenylenediamine in 95% alcohol. Such a solution, prepared from the pure reagent, can be kept indefinitely in a tightly stoppered brown bottle. The solution becomes slightly yellow, but this color does not interfere in the tests.

The reagent solution is prepared when needed by adding 1 ml. of concentrated hydrochloric acid to 100 ml. of the stock solution. In this form the reagent oxidizes slowly and becomes green in color. The oxidized solution is satisfactory for most purposes, but if very small quantities of aldehydes are present it is essential that the reagent be freshly prepared from the stock solution.

If the substance to be tested is a pure compound, the test is carried out by placing two drops in a test tube and adding 5 ml. of the reagent. Aldehydes give an immediate coloration which varies from bright yellow to dark red depending upon the aldehyde. In most cases the color is followed by the appearance of a green fluorescence. Formaldehyde, nitroaldehydes and certain aldehydes which contain conjugated unsaturated linkages such as hexadiene-2,4-al and cinnamaldehyde are the only members tested which did not give fluorescence. This fluorescence can be used not only for the detection of aldehydes but for their differentiation into three classes.

(1) Saturated aliphatic aldehydes. These aldehydes give a light red initial color followed within ten minutes by a bright green fluorescence which becomes stronger on standing and finally completely masks the true color. The strength and rapidity of appearance of the fluorescence increase with the length of the chain up to a maximum at butyraldehyde and then decrease as the number of carbon atoms increases. This series was followed through octaldehyde. Mixed aldehydes such as hydrocinnamaldehyde are included in this class.

Exception: Formaldehyde gives a yellow initial color and no fluorescence.

(2) Unsaturated aliphatic aldehydes. Members of this class give, in general, a darker red initial color than the saturated compounds. The fluorescence appears in a few minutes as in the case of the saturated aldehydes, but instead of being bright green it is a dull brownish-green color. Mixed aldehydes such as alpha-n-amylcinnamaldehyde belong in this class.

Exceptions: Hexadiene-2,4-al and cinnamaldehyde show unusually dark red initial colors, but give no subsequent fluorescence.

(3) Aromatic aldehydes. Members of this class give initial colors which vary from bright yellow to dark red. The chlorine atom and the nitro group decrease the color when substituted in the ring, while the hydroxy, methoxy and dimethylamino groups increase the color. The fluorescence, which is bright green like that of the saturated aliphatics, appears much more slowly and usually can be detected only after two hours or more in the diffused light of the laboratory.

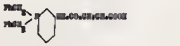
Exceptions: Nitro-aldehydes do not give the fluorescence, but usually precipitate the Schiff bases after standing for twelve hours or more.

Furfuraldehyde can be distinguished from all other aldehydes since it gives a bright red color which changes slowly to dark green on standing. The change is complete at the end of one hour and the color is so deep that observation is facilitated by diluting strongly with alcohol.

The presence of aldehydes as impurities in solvents may be detected by adding 5 ml. of the reagent solution to 10 ml. of the solvent. In no case did the reagent fail to show the presence of 0.01% of the aldehyde in test solutions. Aliphatic aldehydes may be detected in concentrations as low as 0.005% because of the more intense fluorescence which they give in the test. At concentrations of 1% and 0.1% the color appears immediately; however, at 0.01% and lower it is necessary to wait several hours or preferably overnight before comparing with the blank. It is probable that the sensitivity of the test could be increased appreciably by the use of ultraviolet light and by observing the solutions in greater thicknesses. Small amounts of aldehydes may be determined quantitatively by comparison with standards prepared by adding the reagent to portions of the solvent containing known quantities of aldehyde.

Preliminary experiments have shown that this test may be used to advantage for the detection of acetaldehyde in ether. Mallinckrodt[12] has shown that the tests in use at the present for this purpose are unsatisfactory.

The reagent is extremely specific because the color and fluorescence are due to definite compounds formed with the aldehydes and not to their reducing properties. Several members of every important class of compounds were tested, and in only one case did a pure substance which was not an aldehyde give a color reaction with the reagent. This substance was maleic anhydride which acylates the reagent, forming the amide



This is precipitated in the form of a bright yellow powder from a red solution. The color is due to the conjugate system of double bonds. No fluorescence is observed in this case.

Cyclohexanone's weakly positive reaction was accounted for by its splitting in sunlight to form small amounts of the aldehyde

$$CH_2 : CH(CH_2)_3.CHO$$

Unpurified dioxane and diisopropyl ether both contain sufficient aldehydes to give a positive test.

Ketones do not react with the reagent under ordinary conditions.

Chloral was the only aldehyde among those investigated which failed to give a positive test with the reagent. This is because it

does not readily form acetamidines. The para-substituted aromatic aldehydes, which do not give the Schiff test, react normally with the diamine.

Aldehydes used in the development of this test were:

(1) Saturated aliphatic. Formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, hexaldehyde, heptaldehyde, octaldehyde, 2-ethylhexaldehyde, glyoxal, phenylacetaldehyde, hydrocinnamaldehyde, and citronellal.

(2) Unsaturated aliphatic. Acrolein, crotonaldehyde, hexenal-2, 2-vinyl-crotonaldehyde, 2-ethyl-3-propyl-acrolein, hexadiene-2,4-al, cinnamaldehyde, alpha-n-amylcinnamaldehyde, and citral.

(3) Aromatic. Benzaldehyde, salicylaldehyde, anisaldehyde, o-methoxybenzaldehyde, m- and p-tolualdehydes, o-, m-, and p-nitrobenzaldehydes, 2-chloro-5-nitro-benzaldehyde, o- and p-chlorobenzaldehydes, vanillin, veratric aldehyde, piperonal, p-aminobenzaldehyde, p-dimethylaminobenzaldehyde, and p-hydroxybenzaldehyde.

Besides these three main classifications, three heterocyclic aldehydes were tested. These were furfural (discussed on page 29), dibutyraldehyde and dicrotonaldehyde. The last two gave reactions similar to the saturated aliphatic group.

Preparation of the m-dibenzylaminoanilide of Maleic Acid

Five and eight-tenths grams (0.02 mole) of N,N-dibenzyl-m-phenylenediamine was dissolved in 80 cc. of benzene at room temperature. To this solution 2 grams (0.02 mole) of maleic anhydride was added. The solution became red and after stirring for several minutes yellow crystals began separating out. The flask was allowed to remain in the ice-box for ten hours and at the end of that time the precipitate was filtered off, dried and weighed. The yield was 7.5 grams or 98% of theory. The crude product was recrystallized twice from dioxan and dried in an Abderhalden apparatus at 10 mm. Nitrogen analysis showed 7.10% N. Calculated: 7.25% N. The compound did not have a good melting point. It melted slowly with decomposition at temperatures above 180°C. and further attempts at purification failed to improve the melting point.

Properties of the m-Dibenzylaminoanilide of Maleic Acid

Empirical formula	$C_{24}H_{22}N_2O_3$
Structural formula	

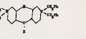
Crystalline form and color	Yellow crystalline powder	
Molecular weight	386.44	
Melting point	188 d.	
Yield	80%	
Analyses	Found	Calculated
Nitrogen	7.18%	7.25%
Solubilities		
Water	Insoluble	
Alcohol	Slightly soluble hot	
Benzene	Soluble hot	
Dioxan	Soluble hot	

PART II

REACTIONS OF ALDEHYDES WITH N,N-DIBENZYL-N'-ACETYL-m-PHENYLENEDIAMINE

Introduction

The purpose of this part of the dissertation originally was to prepare a series of 3,6-bis-dibenzylamino-acridines of formula



in order to study the effect of the heavy benzyl groups on the equilibrium between the orthoquinoid and paraquinoid structures. The existence of such an equilibrium has been shown by Ramart-Lucas, Grumez and Martynoff[13] in spectral absorption studies of acridine yellow, acridine orange, benzoflavine and tetramethylflavosine.

An examination of the means of preparing these compounds revealed that the method most likely to succeed consisted of condensing N,N-dibenzyl-m-phenylenediamine with different aldehydes to form either diphenylmethane or triphenylmethane derivatives, depending upon the nature of the aldehyde used, and the subsequent cyclization of these derivatives to dihydroacridines which, on oxidation, would yield the acridines (see pages 17 and 18).

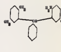
However, the diphenyl- and triphenylmethane derivatives which were prepared as intermediates showed interesting properties and it was decided to make them the object of a separate investigation. Some of the acridines have been prepared and these will be described in a later publication.

Discussion and Review of the Literature

Aldehydes do not react with benzene under ordinary conditions; however, if an ortho-para directing substituent, such as a hydroxyl group or a dimethylamino group, is present in the ring, the hydrogen atoms ortho and para to the substituent are activated. Two molecules of a phenol or an amine can then condense with one molecule of an aldehyde, with the loss of water, to form substituted diphenyl- or triphenylmethanes. Condensing agents most often used are sulfuric acid, hydrochloric acid, anhydrous zinc chloride and phosphorus oxychloride.

If the para position is not occupied the substitution always takes place at that point. However, when para-substituted compounds are used, the entrant group is forced into the ortho position. Ullmann[16] prepared 2,2'-diamino-4,4'-dimethyl-triphenylmethane from p-toluidine and benzaldehyde. He proposed that the aldehyde reacts first with hydrogen atoms from the two amine groups forming an unisolated intermediate having the structure I

I



II

and that the benzylidene group then rearranges, taking the place of an ortho hydrogen atom from each of the two rings. At the same time the two replaced hydrogen atoms must attach themselves at the valence bonds left free by the departure of the benzylidene group. The result is the formation of II which is the only compound isolated.

It seems unnecessary to propose such a mechanism if one takes into account the fact that diethylaniline condenses[15] with aldehydes with equal ease. No such intermediate as I is possible here and if the ortho hydrogen atoms can be substituted directly in this case there is no reason for proposing an intermediate in the case of primary or secondary amines. This is especially true since no such intermediate has ever been isolated.

Of especial interest in the present problem were references to the condensation of m-diamines with aldehydes. When the similar ortho-para directing substituents are located meta to each other in a ring, the two hydrogen atoms which are ortho to one substituent and para to

the other are much more active than usual, since both groups direct to these positions.

Therefore, the two hydrogen atoms marked A in the m-phenylenediamine molecule are very reactive. The hydrogen atom at B is also activated but not to the same extent. The reason for this is evident in view of the fact that groups which direct ortho and para exert most of their influence toward the para position.

Oehler[16] prepared 2,4,2',4'-tetraamino-5,5'-dimethyl-triphenylmethane by heating benzaldehyde with a mixture of m-toluylenediamine and its hydrochloride in alcohol solution. He also prepared the 4"-methyl- and 4"-nitro- derivatives by using p-tolualdehyde and p-nitrobenzaldehyde respectively.

When N,N-dialkyl-m-phenylenediamines are used, the substitution takes place para to the substituted amino group. This is illustrated by the preparation by Sichringer[17] of 3,3'-diamino-4,4'-bis-dimethylamino-diphenylmethane from the dimethyl compound and formaldehyde. There are patents [18] on several other similar reactions.

Since these dialkyl-m-phenylenediamines react smoothly with aldehydes to give substances which are homologous to the desired compounds, no serious difficulties were envisioned in the preparation of these derivatives by similar means from N,N-dibenzyl-m-phenylene-diamine. Accordingly, this compound was prepared by the method

described in Part I. However, the products obtained from the reactions of this compound with aldehydes were not the desired diphenyl- and triphenylmethanes. The reactions gave primarily the Schiff bases and the small amounts of desired compounds formed were cyclized immediately to the corresponding acridines.

The failure of these reactions seemed to be due to the reactivity of the primary amino group. Therefore, the acetyl derivative of the amine was prepared and substituted for the free amine in the reactions. Under these conditions the diacetylated derivatives of the desired products were isolated in yields ranging from 34% to 80%. The benzoyl derivative also was prepared and was found to react similarly. Alpha, beta-unsaturated aldehydes did not react normally and this reaction will be the object of a separate investigation. Preliminary experiments have shown that the diacetylated derivatives lend themselves readily to cyclization to the acridines.

The Preparation of N,N-dibenzyl-N'-acetyl-m-phenylenediamine

This compound was prepared by Desai[8] and by Bayer and Co.[9]. No experimental procedure was given by either.

One hundred and forty-four grams ($\frac{1}{2}$ mole) of N,N-dibenzyl-m-phenylenediamine was placed in a 500 cc. round-bottomed flask which was immersed in an ice-bath. Two hundred and four grams (2 moles) of acetic anhydride was allowed to flow very slowly with constant shaking into the flask. The rate of addition was such that the temperature did not rise above 60°C. The reaction mixture became soft and then solidified. This solid mass of white crystals was broken up thoroughly and allowed to remain in contact with the excess acetic anhydride overnight. Most of the excess was removed by decantation and the remainder was hydrolyzed by suspending the product in hot water. The acetylated compound was filtered off and recrystallized from dilute alcohol. After drying in a vacuum desiccator over concentrated sulfuric acid the product weighed 158 grams. This is 96% of the theoretical yield. The melting point was 144-145°C. which agrees well with the results of the the previous investigators (145-46°C.). Further crystallizations failed to raise the melting point. Nitrogen analysis showed 8.41% N. Calculated: 8.48% N.

The Preparation of N,N-Dibenzyl-N'-benzoyl-m-phenylenediamine

This compound was prepared by Desai[8] who gave an experimental procedure.

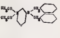
Fourteen and four-tenths grams (1/20 mole) of N,N-dibenzyl-m-phenylenediamine was suspended in 200 cc. of 10% sodium hydroxide solution and 28 grams (1/5 mole) of benzoyl chloride was added. The mixture was shaken for half an hour and then allowed to remain at room temperature for several hours. The flocculent white crystals were filtered off and washed several times with water and then twice with alcohol. Recrystallization from alcohol gave 17.6 grams (90% of theory) of a very pure product melting at 171°C. Desai reported 171-172°C. Analysis showed 7.16% N. Calculated: 7.14% N.

The Preparation of N,N-Dibenzyl-N',N'-diacetyl-m-phenylenediamine.

Sixteen and five-tenths grams (0.05 mole) of N,N-dibenzyl-N'-acetyl-m-phenylenediamine, 8.2 grams (0.10 mole) of anhydrous sodium acetate and 102 grams (1.0 mole) of acetic anhydride were refluxed together for five hours. The reaction mixture was poured over cracked ice and allowed to stand with occasional stirring until all the excess acetic anhydride was decomposed and the diacetyl compound separated out as a white flocculent precipitate. This was filtered off and washed first with water and then with alcohol and finally was recrystallized from 95% alcohol. The crystals, which were in the form of very small needles, were dried in an Abderhalden apparatus at 100°C. over sulfuric acid at 10 mm. pressure. The yield was 16.8 grams or 90% of the theoretical. Nitrogen analysis showed 7.48% N. Calculated: 7.53% N. The melting point of the pure substance was 152°C.

The Properties of N,N-Dibenzyl-N',N'-diacetyl-p-phenylenediamine

Empirical formula	$C_{24}H_{24}N_2O_2$
Structural formula	



Crystalline form and color	White needles	
Molecular weight	372.41	
Melting point	152°C.	
Yield	60%	
Analyses	Found	Calculated
Nitrogen	7.60%	7.52%
Solubilities		
Water	Insoluble	
Alcohol	Soluble hot	
Acetone	Soluble	
Dioxane	Soluble	
Acetic acid	Soluble	

EXPERIMENTAL TABLES AND PROCEDURES

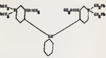
1. Preparation of 2,2'-bis-acetamino-4,4'-bis-dibenzylamino-triphenylmethane.

Five grams (0.015 mole) of N,N-dibenzyl-N'-acetyl-m-phenylenediamine was dissolved in 50 ml. of hot alcohol then 3 grams (0.0075 mole) of 20% sulfuric acid and 0.8 grams (0.0075 mole) of benzaldehyde were added. This solution was heated under reflux on the steam bath. After about fifteen minutes the solution became light green in color and at the end of an hour a mass of white crystals was precipitated from the solution which at the end of this time was dark green. The heating was continued for two more hours and then about half of the alcohol was distilled off the the flask was placed in the refrigerator and allowed to remain overnight. There was further crystallization during the night. The crystals were filtered off and washed with alcohol in which they are insoluble in the cold and only very slightly soluble at the boiling point. These crystals when dry weighed only 1.2 grams, indicating the possibility that there was an appreciable quantity remaining in the mother liquor. This was poured over chipped ice and after the ice had melted there remained a yellow resinous mass which showed a decided tendency to turn green on standing in the air. This amorphous material was heated with 50 ml. of 95% alcohol the most of it dissolved leaving a residue of white crystals which were shown by a mixed melting point to be identical with the compound isolated above. These two portions were combined, extracted with hot alcohol the

recrystallized from dilute dioxan. The yield was 5.7 grams or 60% of the theoretical. The sample was dried in a vacuum desiccator over solid potassium hydroxide. Nitrogen analysis showed 7.61% N. Calculated: 7.66% N. The melting point was 225° C.

1. 3,3'-Bis-acetamino-4,4'-bis-dibenzylamino-triphenylmethane

Empirical formula	$C_{51}H_{48}N_4O_2$
Structural formula	



Crystalline form and color	White powder	
Molecular weight	748.42	
Melting point	230°C.	
Yield	40%	
Analyses	Found	Calculated
Nitrogen	7.48%	7.48%
Solubilities		
Water	Insoluble	
Alcohol	Slightly soluble hot	
Acetone	Soluble hot	
Acetic acid	Soluble hot	
Dioxan	Soluble hot	

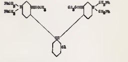
2. Preparation of 2,2'-bis-acetamino-4,4'-bis-dibenzylamino-2''-chloro-triphenylmethane.

Five grams (0.015 mole) of N,N-dibenzyl-N'-acetyl-m-phenylenediamine was dissolved in 50 ml. of hot alcohol and 8 grams (0.0075 mole) of 80% sulfuric acid and 1.05 grams (0.0075 mole) of o-chlorobenzaldehyde were added whereupon the solution became slightly yellow. Subsequent refluxing on the steam bath yielded a green solution after ½ hour and a sandy white precipitate after three hours. About half of the alcohol was distilled off after two more hours of heating and the flask was allowed to remain in the refrigerator overnight. There was very little if any further precipitation and the crystals were filtered off. In order to recover any of the substance which remained dissolved the mother liquor was poured into a large quantity of water and allowed to stand for an hour after which it was filtered and heated with 20 ml. of acetic anhydride for thirty minutes in order to reacetylate any of the compound which might have been hydrolyzed during the reaction. An excess of alcohol was then added and the solution was boiled to decompose the acetic anhydride. The flask was allowed to remain in the ice-box overnight and an additional quantity of crystals amounting to 1.2 grams was filtered off. The total yield was 3.9 grams or 64% of the theoretical. In order to purify the sample for analysis it was first extracted with boiling alcohol, then recrystallized from acetic acid, washed with alcohol and finally recrystallized from dilute dioxane. It was dried in a vacuum desiccator over solid KOH. Nitrogen analysis showed 7.08% N. Calculated: 7.14% N. The melting point of the pure substance was 242°C.

2. 2,2'-Bis-acetamino-4,4'-bis-dibenzylamino-4''-chloro-triphenylmethane.

Empirical formula $C_{51}H_{47}N_4O_2Cl$

Structural formula



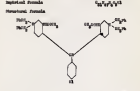
Crystalline form and color	White powder
Molecular weight	783.34
Melting point	242°C.
Yield	60%
Analyses	Found Calculated
Nitrogen	7.02% 7.14%
Solubilities	
Water	Insoluble
Alcohol	Very slightly soluble hot
Acetone	Soluble hot
Acetic acid	Soluble hot
Dioxan	Soluble hot

8. Preparation of 2,2'-bis-acetamino-4,4'-bis-dibenzylamino-4''-chloro-triphenylmethane.

Six and six-tenths grams (0.02 mole) of N,N-dibenzyl-N'-acetyl-m-phenylenediamine was dissolved in 200 ml. of 95% alcohol and 4.2 grams (0.03 mole) of p-chlorobenzaldehyde and 1 gram (0.01 mole) of concentrated sulfuric acid were added. The solution was refluxed for four hours on the steam bath. A light green coloration appeared almost immediately and after forty-five minutes white crystals began to precipitate. After the end of the four hours of refluxing, the flask was placed in the refrigerator and allowed to remain overnight. The white precipitate was filtered off, washed with alcohol, extracted with hot alcohol and recrystallized twice from dilute dioxane. After drying in a vacuum desiccator over solid KOH the yield was 4.2 grams or 54% of the theoretical. Analysis for nitrogen showed 7.09% N. Calculated: 7.14% N. The melting point was 248°C.

5. 3,3'-Bis-acetamino-4,4'-bis-dibenzylamino-4''-chloro-triphenylmethane

Empirical formula	$C_{51}H_{47}N_4O_2Cl$
Structural formula	



Crystalline form and color	White powder	
Molecular weight	782.86	
Melting point	240°C.	
Yield	80%	
Analyses	Found	Calculated
Nitrogen	7.08%	7.14%
Solubilities		
Water	Insoluble	
Alcohol	Very slightly soluble hot	
Acetone	Soluble hot	
Acetic acid	Soluble hot	
Dioxan	Soluble hot	

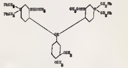
6. Preparation of 2,2'-bis-acetamino-4,4'-bis-dibenzylamino-3",4"-dimethoxy-triphenylmethane.

Ten grams (0.030 mole) of N,N-dibenzyl-N'-acetyl-m-phenylenediamine was dissolved in 100 ml. of hot 95% alcohol and six grams (0.018 mole) of 95% sulfuric acid and 2.6 grams (0.015 mole) of veratric aldehyde were added. The colorless solution was refluxed on the steam bath and at the end of twenty minutes it was dark green. After four and one-half hours sandy white crystals were precipitated and the heating was continued for an additional two hours after which the flask was placed in the refrigerator and allowed to remain overnight. The crystals were filtered off with suction and were found to weigh five and nine-tenths grams. The filtrate was treated in the cold with fifteen grams of acetic anhydride in order to reacetylate any of the compound which might have been hydrolyzed during the reaction. This solution was poured over crushed ice and the resulting resinous mass was recrystallized the following day from dioxane and yielded 0.7 gram of white crystals which were shown by mixed melting point to be identical with the substance isolated above. The total yield was 6.6 grams or 54% of the theory. The two yields were combined and recrystallized twice from dilute dioxane followed by extraction with boiling alcohol. The substance was dried in an Abderhalden drier over concentrated sulfuric acid and nitrogen analysis showed 8.38% N. Calculated: 8.58% N. The melting point of the pure substance was 231°C.

6. 2,2'-bis-acetamino-4,4'-bis-dibenzylamino-3",4"-dimethoxy-triphenylmethane.

Empirical formula $C_{53}H_{52}N_4O_4$

Structural formula



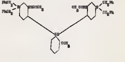
Crystalline form and color	White leaflets	
Molecular weight	808.42	
Melting point	231° C.	
Yield	54%	
Analysis	Found	Calculated
Nitrogen	6.83%	6.93%
Solubilities		
Water	Insoluble	
Alcohol	Very slightly soluble hot	
Acetone	Soluble hot	
Acetic acid	Soluble hot	
Dioxan	Soluble hot	

5. Preparation of 2,2'-bis-acetamino-4,4'-bis-dibenzylamino-2''-methoxy-triphenylmethane.

Ten grams (0.030 mole) of N,N-dibenzyl-N'-acetyl-m-phenylenediamine, 6 grams (0.015 mole) of 25% sulfuric acid and 2.04 grams (0.015 mole) of o-methoxybenzaldehyde were dissolved in 200 ml. of hot 95% alcohol and heated in a sealed tube at 100°C. The solution became light green immediately and darker green progressively as the heating was continued until at the end of about two hours a large quantity of sandy white crystals was precipitated. The tube was heated for two more hours and then was allowed to cool and was opened and the crystals filtered off. These were crystallized twice from dilute dioxane and then extracted with boiling alcohol, filtered, and dried in an Abderhalden drier. The yield was 7.8 grams or 67% of the theoretical. Analysis showed 7.10% N. Calculated: 7.10% N. The melting point of the pure substance was 244°C.

8. 2,2'-Bis-acetamino-4,4'-bis-dibenzylamino-2''-methoxy-triphenylmethane

Empirical formula	$C_{52}H_{50}N_4O_3$
Structural formula	



Crystalline form and color	White crystalline powder	
Molecular weight	778.44	
Melting point	244°C.	
Yield	67%	
Analyses	Found	Calculated
Nitrogen	7.19%	7.20%
Solubilities		
Water	Insoluble	
Alcohol	Very slightly soluble hot	
Acetone	Slightly soluble hot	
Acetic acid	Soluble hot	
Dioxan	Soluble hot	

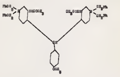
6. Preparation of 2,2'-bis-acetamino-4,4'-bis-dibenzylamino-4"-methoxy-triphenylmethane.

Five grams (0.015 mole) of N,N-dibenzyl-N'-acetyl-m-phenylenediamine, 5 grams (0.0076 mole) of 98% sulfuric acid and 1.27 grams (0.013 mole) of anisaldehyde were dissolved in 50 ml. of alcohol and refluxed for five hours on the steam bath. During this time the solution became purple. No precipitate was formed on standing overnight in the icebox so the solution was treated with ten grams of acetic anhydride in the cold for three hours and then was poured over cracked ice. The grey crystals which resulted after standing for twenty-four hours were unstable in the air and turned purple rapidly. In attempting to extract the impurities from these crystals with hot alcohol a peculiar phenomenon was observed. On primary contact with the hot alcohol the substance melted to a dark oil and then suddenly crystallized in the form of a white powder which was very insoluble in the alcohol. The solution above the crystals showed very strong green fluorescence, indicating cyclization to the acridine derivative of an appreciable part of the triphenylmethane derivative. The crystals were filtered off and after drying were found to weigh 2.3 grams which represents 40% of the theoretical yield. After recrystallizing first from acetic acid and then from dilute dioxane and extracting with boiling alcohol analysis showed 7.11% N. Calculated: 7.20% N. The melting point of the pure compound was 236°C.

6. 2,2'-Bis-acetamino-4,4'-bis-dibenzylamino-4''-methoxy-triphenylmethane.

Empirical formula $C_{52}H_{50}N_4O_3$

Structural formula



Crystalline form and color	White crystalline powder
Molecular weight	778.66
Melting point	224°C.
Yield	40%
Analysis	Found Calculated
Nitrogen	7.11% 7.20%
Solubilities	
Water	Insoluble
Alcohol	Very slightly soluble hot
Acetone	Slightly soluble hot
Acetic acid	Soluble hot
Dioxan	Soluble hot

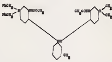
7. Preparation of 2,2'-bis-acetamino-4,4'-dibenzylamino-3"-methyltriphenylmethane.

Ten grams (0.030 mole) of N,N-dibenzyl-N'-acetyl-m-phenylenediamine, 1.8 grams (0.015 mole) of m-tolualdehyde and 6 grams (0.015 mole) of 25% sulfuric acid were dissolved in 100 ml. of alcohol and refluxed for a total of six hours on the steam bath. The solution became green almost immediately and after three and one-half hours there was precipitation of white crystals. These were filtered off and dried. The yield was 8.2 grams or 36% of the theory. In this case no attempt was made to recover anything from the filtrate. After purification by extraction with hot alcohol and recrystallization from dilute dioxan followed by recrystallization from glacial acetic acid and a second alcohol extraction, the melting point was found to be 215°C. The analytical sample was dried in an Abderhalden apparatus for two hours over sulfuric acid at 20 mm. and 100°C. Analysis showed 7.30% N. Calculated: 7.34% N.

V. 2,2'-Bis-acetamino-4,4'-bis-dibenzylamino-3''-methyl-triphenylmethane.

Empirical formula $C_{52}H_{50}N_4O_2$

Structural formula



Crystalline form and color	Sandy white crystals
Molecular weight	762.40
Melting point	216°C.
Yield	80%
Analysis	Found Calculated
Nitrogen	7.30% 7.35%
Solubilities	
Water	Insoluble
Alcohol	Very slightly soluble hot
Acetone	Slightly soluble hot
Acetic acid	Soluble hot
Dioxan	Soluble hot

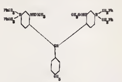
8. Preparation of 2,2'-bis-acetamino-4,4'-bis-dibenzylamino-4''-methyl-triphenylmethane.

Ten grams (0.030 mole) of N,N-dibenzyl-N'-acetyl-m-phenylenediamine, 1.8 grams (0.015 mole) of p-tolualdehyde and 6 grams (0.015 mole) of 50% sulfuric acid were dissolved in 100 ml. of hot alcohol and refluxed on the steam bath. The solution turned dark green almost immediately and after one hour and forty-five minutes there was precipitation of white crystals. Refluxing was continued for another hour and a half and then the flask was allowed to remain in the refrigerator overnight. The crystals were filtered off and dried and weighed. The yield was 7.3 grams or 68% of the theory. The crude product was purified by extraction with boiling alcohol followed by two recrystallizations from dilute dioxane. The pure substance was dried in an Abderhalden apparatus after which nitrogen analysis showed 7.28% N. Calculated: 7.36% N. The melting point determination on the Maquenne block showed the unusual double melting point phenomenon. If the crystals are placed on the block when the temperature is below 218°C. they melt sharply at 220°C. However, if they are put on the block when the thermometer reads between 218°C. and 226°C. they melt quickly and then slowly recrystallize on the block. If the temperature is then allowed to rise slowly the substance melts sharply at 220°C., the original melting point. Finally, if the temperature of the block is above 226°C. when the substance is applied, melting occurs immediately and

there is no subsequent solidification. When this melting point was taken by the conventional capillary tube method, the melting point was found to be 128°C. after addition of the stem correction. However, the double melting point was observed just as in the case where the Maquenne block was used if precautions were taken to immerse the substance only when the correct temperatures had been reached.

8. 2,2'-Bis-acetamino-4,4'-bis-dibenzylamino-4''-methyl-triphenylmethane.

Empirical formula	$C_{52}H_{50}N_4O_2$
Structural formula	



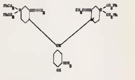
Crystalline form and color	White crystalline powder	
Molecular weight	762.40	
Melting point	218 °C.	
Yield	68%	
Analyses	Found	Calculated
Nitrogen	7.32%	7.35%
Solubilities		
Water	Insoluble	
Alcohol	Very slightly soluble hot	
Acetone	Slightly soluble hot	
Acetic acid	Soluble hot	
Dioxane	Soluble hot	

9. Preparation of 2,2'-bis-acetamino-4,4'-bis-dibenzylamino-3"-methoxy-4"-hydroxy-triphenylmethane.

Thirteen and two-tenths grams (0.04 mole) of N,N-dibenzyl-N'-acetyl-m-phenylenediamine, 3.1 grams (0.02 mole) of vanillin and 2.0 grams (0.02 mole) of concentrated sulfuric acid were dissolved in 200 ml. of alcohol and heated under reflux for four hours on the steam bath. During this time the solution became deep red in color but no precipitate was formed. However, on standing in the refrigerator for several days a precipitate of gray crystals slowly formed in the bottom of the flask. This was filtered off at the pump, washed with alcohol and dried. The yield was 7.7 grams or 48% of theory. During the drying the compound became purple very rapidly and all attempts at purification failed to yield a colorless product. The crude substance was recrystallized twice from alcohol, in which it is much more soluble than the other members of this series (influence of the hydroxyl group), and dried in vacuo over solid potassium hydroxide after which nitrogen analysis showed 6.88% N. Calculated: 7.05% N. The melting point, which did not change appreciably with degree of oxidation, was 196°C.

9. 2,2'-bis-acetamino-4,4'-bis-dibenzylamino-3''-methoxy-4''-hydroxy-triphenylmethane.

Empirical formula	$C_{52}H_{50}N_4O_4$
Structural formula	



Crystalline form and color	White powder	
Molecular weight	794.44	
Melting point	188°C.	
Yield	40%	
Analyses	Found	Calculated
Nitrogen	6.95%	7.05%
Solubilities		
Water	Insoluble	
Alcohol	Soluble hot	
Acetone	Soluble hot	
Acetic acid	Soluble	
Dioxane	Soluble	

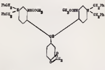
10. Preparation of 2,2'-bis-acetamino-4,4'-bisdibenzylamino-3",4"-methylenedioxy-triphenylmethane.

Six and six-tenths grams (0.02 mole) of N,N-dibenzyl-N'-acetyl-m-phenylenediamine, 1.5 grams (0.01 mole) of piperonal and 8 grams (0.025 mole) of 25% sulfuric acid were dissolved in seventy ml. of hot alcohol and refluxed on the steam bath. The solution turned very dark almost immediately and after two and one-half hours of heating a finely divided white precipitate was deposited. Refluxing was continued for an additional two and one-half hours after which the flask was allowed to remain overnight in the refrigerator. Filtration followed by drying gave a yield of 3.5 grams which represents 44% of the theoretical. The yield was undoubtedly decreased because of the use of a smaller amount of the acid than usual. The crude product was purified by the recrystallizations from dilute dioxan followed by extraction with alcohol. In recrystallizing the substance was dissolved in dioxan at the boiling point and then water was added until separation began, after which the cloudiness was cleared up by addition of more hot dioxan and the compound was allowed to crystallize slowly from the saturated solution. The solution in anhydrous dioxan was colorless or pale yellow, but on addition of water it changed to a beautiful violet color. After drying in an Abderhalden apparatus analysis showed 6.98% N. Calculated: 7.07% N. The melting point of the pure substance was 255°C.

10. 2,2'-Bis-acetamino-4,4'-bis-dibenzylamino-3",4"-methylenedioxy-triphenylmethane.

Empirical formula $C_{52}H_{48}N_4O_4$

Structural formula



Crystalline form and color	White leaflets	
Molecular weight	792.45	
Melting point	225°C.	
Yield	64%	
Analyses	Found	Calculated
Nitrogen	6.85%	7.07%
Solubilities		
Water	Insoluble	
Alcohol	Very slightly soluble hot	
Acetone	Slightly soluble hot	
Acetic acid	Soluble hot	
Dioxan	Soluble hot	

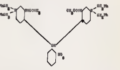
11. Preparation of 2,2'-bis-acetamino-4,4'-bis-dibenzylamino-2''-nitro-triphenylmethane.

Two grams (0.006 mole) of N,N-dibenzyl-2'-acetyl-m-phenylenediamine, 0.5 grams (0.003 mole) of o-nitrobenzaldehyde and 8 grams (0.015 mole) of 30% sulfuric acid were dissolved in 150 ml. of alcohol and heated in a sealed tube at 100°C. for three hours. At the end of this time there had been no precipitation so the contents of the tube were poured over cracked ice and allowed to stand in the refrigerator for 24 hours. The semi-resinous solid was filtered off and extracted with hot alcohol, which left a yellow crystalline residue. This was recrystallized from dilute dioxan and after drying the yield was found to be 0.4 grams or 64% theory. At this point a melting point was taken and the partially purified substance melted at 227°C. After recrystallizing again from a mixture of equal parts of dioxan and alcohol the melting point was 228°C. Another recrystallization from the same solvent pair failed to raise the melting point. After drying in an Abderhalden apparatus nitrogen analysis showed 8.78% N. Calculated: 8.82% N.

11. 2,2'-bis-acetamino-4,4'-bis-dibenzylamino-4''-nitro-triphenylmethane.

Empirical formula $C_{51}H_{47}N_5O_4$

Structural formula



Crystalline form and color	Yellow leaflets[a]	
Molecular weight	793.45	
Melting point	226°C.	
Yield	46%	
Analysis	Found	Calculated
Nitrogen	8.70%	8.82%
Solubilities		
Water	Insoluble	
Alcohol	Slightly soluble	
Acetone	Slightly soluble	
Acetic acid	Soluble	
Dioxan	Soluble	

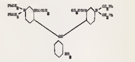
12. Preparation of 2,2'-bis-acetamino-4,4'-bis-dibenzylamino-3''-nitro-triphenylmethane.

Six and six-tenths grams (0.030 mole) of N,N-dibenzyl-N'-acetyl-m-phenylenediamine, 2.0 grams (0.02 mole) of concentrated sulfuric acid and 2.6 grams (0.02 mole) of m-nitrobenzaldehyde were dissolved in 250 ml. of 95% alcohol and heated on the steam bath for five hours. During this time there was no precipitation but the solution became yellow and finally a yellow-red color. Upon standing overnight in the refrigerator only a very small quantity of crystalline material was deposited, so the solution was poured over cracked ice and salt was added to keep the substance from remaining in solution in the colloidal state. After twenty-four hours the resinous solid was filtered off and extracted with alcohol at the boiling point which left a crystalline residue which was further purified by recrystallization from dilute dioxan and another extraction with hot alcohol. The yield was 4.8 grams or 60% of the theory. A sample for analysis was recrystallized again from dioxan and dried in the Abderhalden apparatus. Analysis showed 8.90% N. Calculated: 8.85% N. The melting point of the pure substance was found to be 211°C.

12. 2,2'-Bis-acetamino-4,4'-bis-dibenzylamino-3"-nitro-triphenylmethane.

Empirical formula $C_{51}H_{47}N_5O_4$

Structural formula



Crystalline form and color	Yellow leaflets	
Molecular weight	793.93	
Melting point	211°C.	
Yield	60%	
Analyses	Found	Calculated
Nitrogen	8.78%	8.82%
Solubilities		
Water	Insoluble	
Alcohol	Very slightly soluble hot	
Acetone	Slightly soluble hot	
Dioxane	Soluble hot	
Acetic acid	Soluble hot	

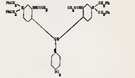
15. Preparation of 2,2'-bis-acetamino-4,4'-bis-dibenzylamino-4''-nitro-triphenylmethane.

Five grams (0.015 mole) of N,N-dibenzyl-N'-acetyl-m-phenylenediamine, 1.6 grams (0.011 mole) of p-nitrobenzaldehyde and 8 grams (0.0078 mole) of 28% sulfuric acid were dissolved in 60 ml. of 95% alcohol and heated in a sealed tube at 100°C. for three and one-half hours. During this time there was precipitation of a yellow crystalline powder. The contents of the tube were treated with ten ml. of acetic anhydride in order to reacetylate any of the amine which had been hydrolyzed during the reaction. After heating to boiling in order to decompose the excess acetic anhydride the solution was poured over cracked ice and allowed to remain in the refrigerator overnight. Upon filtration a yellow solid was obtained which seemed amorphous and which was difficult to free from excess water. However, extraction with hot alcohol left a finely crystalline residue which was further purified by recrystallization from dioxane. After drying the yield was found to be 6.0 grams or 70% of the theoretical. The analytical sample was recrystallized again from dioxane, extracted with hot alcohol and dried in an Abderhalden apparatus. Nitrogen analysis showed 8.30% N. Calculated: 8.83% N. The melting point of the pure product was found to be 261°C.

15. 3,3'-Bis-acetamino-4,4'-bis-dibenzylamino-4''-nitro-triphenylmethane.

Empirical formula $C_{51}H_{47}N_5O_4$

Structural formula



Crystalline form and color	Yellow leaflets	
Molecular weight	793.95	
Melting point	231°C.	
Yield	70%	
Analyses	Found	Calculated
Nitrogen	8.80%	8.82%
Solubilities		
Water	Insoluble	
Alcohol	Very slightly soluble hot	
Acetone	Slightly soluble hot	
Acetic acid	Soluble hot	
Dioxan	Soluble hot	

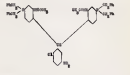
14. Preparation of 2,2'-bis-acetamino-4,4'-bis-dibenzylamino-2"-chloro-5"-nitro-triphenylmethane.

Six and six-tenths grams (0.02 mole) of N,N-dibenzyl-N'-acetyl-m-phenylenediamine, 2.8 grams (0.02 mole) of 2-chloro-5-nitro-benzaldehyde and 1 gram (0.01 mole) of concentrated sulfuric acid were dissolved in 250 ml. of 95% alcohol and refluxed for six hours on the steam bath. During this time the color of the solution changed from pale yellow to bright yellow but no crystals were deposited. After cooling, the contents of the flask were treated with 15 grams of acetic anhydride in order to reacetylate any of the substance which had been hydrolyzed during the reaction. The solution was allowed to remain in the refrigerator overnight and the yellow precipitate which separated out during the night was filtered off. After drying this was found to weigh 6.3 grams which represents 64% of the theoretical yield. The sample for analysis was extracted with alcohol and then recrystallized twice from dilute dioxane. It was dried in a vacuum desiccator over solid KOH. Analysis for nitrogen showed 8.42% N. Calculated: 8.48% N. The melting point of the pure substance was 240°C.

14. 2,2'-Bis-acetamino-4,4'-bis-dibenzylamino-2"-chloro-5"-nitro-triphenylmethane.

Empirical formula $C_{51}H_{45}N_5O_4Cl$

Structural formula



Molecular weight	827.38
Crystalline form and color	Yellow leaflets
Melting point	240° C.
Yield	64%
Analyses	Found Calculated
Nitrogen	8.32% 8.38%
Solubilities	
Water	Insoluble
Alcohol	Slightly soluble hot
Acetone	Slightly soluble hot
Acetic acid	Soluble hot
Dioxan	Soluble hot

16. Preparation of bis-(3-amino-4-dibenzylamino)-diphenylmethane.

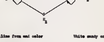
Two and nine-tenths grams (0.01 mole) of N,N-dibenzyl-m-phenylenediamine was dissolved in a mixture of 500 cc. of water and 10 cc. of concentrated hydrochloric acid. Solution is effected more easily by heating to 80°C. The solution was cooled to 0°C. Three and seven-tenths grams (0.005 mole) of 4% formaldehyde solution was dissolved in 50 ml. of ice-water and added drop-wise to the cooled solution described above. Shaking was maintained during the addition and the temperature was kept below 5°C. The flask was placed in the refrigerator and allowed to remain for two weeks. During this time well-defined, sandy crystals separated out and adhered to the sides of the flask. These were filtered off and dried and weighed. The yield was 2.0 grams or 70% of theory. The crude product was recrystallized twice from alcohol and dried in an Abderhalden drier. Nitrogen analysis showed 9.47% N. Calculated 9.52% N. The melting point of the pure substance was 132°C.

If the conditions of temperature and dilution given above are not followed exactly, a yellow, amorphous polymer is obtained from the reaction.

15. Bis-(3-amino-4-dibenzylamino)-diphenylmethane.

Empirical formula $C_{41}H_{40}N_4$

Structural formula



Crystalline form and color	White sandy crystals
Molecular weight	588.36
Melting point	165°C.
Yield	70%
Analyses	Found Calculated
Nitrogen	9.47% 9.58%
Solubilities	
Water	Insoluble
Alcohol	Soluble hot
Acetone	Soluble hot
Acetic acid	Soluble
Dioxan	Soluble

16. Preparation of bis-(2-acetamino-6-dibenzylamino)-diphenylmethane.

Two and five-tenths grams (0.0075 mole) of N,N-dibenzyl-N'-acetyl-m-phenylenediamine, 1.5 grams (0.0088 mole) of 38% sulfuric acid and 10 ml. (a large excess) of approximately 40% formaldehyde solution were dissolved in 50 ml. of 45% alcohol and heated in a sealed tube at 100°C. for three hours. During this time there was slow precipitation of white crystals from the colorless solution. After cooling in the refrigerator, the tube was opened and the crystals filtered off, washed with alcohol and digested with 50 ml. of boiling alcohol. After drying the crystals weighed 1.5 grams which represents 75% of the theoretical yield. The analytical sample was recrystallized from dioxane and dried in a vacuum desiccator over solid KOH. Analysis for nitrogen showed 8.10% N. Calculated; 8.33% N. The melting point of the pure compound was 241°C.

This compound was also prepared by acetylating bis-(2-amino-6-dibenzylamino)-diphenylmethane. This was accomplished by refluxing one gram of the compound in a solution composed of 5 ml. of acetic acid and 1 ml. of acetic anhydride. The solution was poured into ice water and The white crystals which separated on standing were recrystallized from dioxane. A mixed melting point showed that the two materials isolated were identical.

16. Bis-(3-acetamino-4-dibenzylamino)-diphenylmethane.

Empirical formula	$C_{45}H_{44}N_4O_2$
Structural formula	

Crystalline form and color	White powder	
Molecular weight	672.80	
Melting point	241°C.	
Yield	72%	
Analyses	Found	Calculated
Nitrogen	8.10%	8.33%
Solubilities		
Water	Insoluble	
Alcohol	Slightly soluble hot	
Acetone	Slightly soluble hot	
Acetic acid	Soluble hot	
Dioxane	Soluble hot	

17. Preparation of bis-(2-acetamino-4-dibenzylamino)-diphenyl-methyl-methane.

Six and six-tenths grams (0.02 mole) of N,N-dibenzyl-N'-acetyl-m-phenylenediamine, 2.6 grams (the equivalent of 0.06 mole of acetaldehyde) of paraldehyde, and 1.0 gram (0.01 mole) of concentrated sulfuric acid were dissolved in 100 ml. of 95% alcohol and heated in a sealed tube at 75°C. for four hours. After cooling, the tube was opened and the contents, which consisted of a pale red solution, were poured over cracked ice. After several hours the resulting resinous yellow mass was filtered off and extracted with alcohol, which left the product behind as white crystals. The yield was 5.2 grams or 76% of the theoretical. The sample for analysis was recrystallized twice from dioxane and nitrogen analysis, after drying in a vacuum desiccator over solid KOH, showed 8.08% N. Calculated: 8.17% N. The melting point of the pure substance was 178°C.

17. Bis-(3-acetamino-4-dibenzylamino)-diphenyl-methyl-methane.

Empirical formula $C_{46}H_{46}N_4O_2$

Structural formula

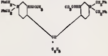
Crystalline form and color	White powder	
Molecular weight	686.41	
Melting point	172°C.	
Yield	70%	
Analyses	Found	Calculated
Nitrogen	8.08%	8.17%
Solubilities		
Water	Insoluble	
Alcohol	Slightly soluble hot	
Acetone	Soluble hot	
Acetic acid	Soluble hot	
Dioxane	Soluble hot	

16. Preparation of bis-(2-acetamino-4-dibenzylamino)-diphenyl-ethyl-methane.

Five grams (0.015 mole) of N,N-dibenzyl-N'-acetyl-m-phenylenediamine, 10 ml. (a large excess) of propionaldehyde and 5 grams (0.0075 mole) of 20% sulfuric acid were heated in a sealed tube at 100°C. At the end of two hours of heating, a mass of white crystals suddenly separated from the solution. The heating was continued for an hour after which the tube was cooled and opened. The crystals were filtered off with suction and dried. The yield was 3.0 grams or 57% of the theoretical. The analytical sample was extracted with alcohol and then was recrystallized twice from dioxane. After drying in an Abderhalden apparatus nitrogen analysis showed 7.81% N. Calculated: 8.00% N. The melting point of the pure substance was 236°C.

18. Bis-(2-acetamino-4-dibenzylamino)-diphenyl-ethyl-methane.

Empirical formula	$C_{47}H_{46}N_4O_2$
Structural formula	



Crystalline form and color	White powder	
Molecular weight	700.4	
Melting point	250°C.	
Yield	87%	
Analyses	Found	Calculated
Nitrogen	7.81%	8.00%
Solubilities		
Water	Insoluble	
Alcohol	Slightly soluble hot	
Acetone	Soluble hot	
Acetic acid	Soluble hot	
Dioxan	Soluble hot	

19. Preparation of bis-(2-acetamino-4-dibenzylamino)-diphenyl-n-propyl-methane.

Six and six-tenths grams (0.02 mole) of N,N-dibenzyl-N'-acetyl-m-phenylenediamine, 2.2 grams (0.03 mole) of butyraldehyde and 1.0 gram (0.01 mole) of concentrated sulfuric acid were dissolved in 200 ml. of 95% alcohol and refluxed on the steam bath. The solution became light yellow on heating and after four hours a crystalline precipitate separated out. The flask was allowed to remain in the refrigerator overnight. The crystals were filtered off and dried. The yield was 2.5 grams or 36% of the theoretical. The analytical sample was extracted with hot alcohol and later was recrystallized twice from dioxane. After drying in an Abderhalden apparatus, nitrogen analysis showed 7.03% N. Calculated: 7.04% N. The melting point of the pure substance was 265°C.

19. Bis-(2-acetamino-5-dibenzylamino)-diphenyl-n-propyl-methane.

Empirical formula	$C_{46}H_{50}N_4O_2$
Structural formula	

Crystalline form and color	White powder	
Molecular weight	712.44	
Melting point	248°C.	
Yield	60%	
Analysis	Found	Calculated
Nitrogen	7.82%	7.86%
Solubilities		
Water	Insoluble	
Alcohol	Slightly soluble hot	
Acetone	Soluble hot	
Acetic acid	Soluble hot	
Dioxane	Soluble hot	

20. Preparation of bis-(2-acetamino-4-dibenzylamino)-diphenyl-n-amyl-methane.

Five grams (0.015 mole) of N,N-dibenzyl-N'-acetyl-m-phenylenediamine, 8.0 grams (0.0075 mole) of 25% sulfuric acid and 1.0 gram (0.01 mole) of benzaldehyde were dissolved in 60 ml. of 95% alcohol and heated in a sealed tube at 100° C. for four hours. During this time the solution became dark red in color and showed an extremely strong green fluorescence, indicating partial condensation to the acridine derivative. the tube was allowed to cool, and then was opened and the solution allowed to evaporate at room temperature. A red resin was obtained as the main product but in this could be seen well-formed white crystals. Several extractions with boiling alcohol left the white crystals, which are practically insoluble in alcohol, free from the resinous material. The yield was 1.4 grams or 28% of theory. The sample for analysis was recrystallized twice from dioxan and again from a mixture of equal parts of benzene and heptane. After drying in the Abderhalden apparatus, nitrogen analysis showed 7.44% N, calculated: 7.86% N. The melting point of the pure substance was 201°C.

20. Bis-(2-acetamino-5-dibenzylamino)-diphenyl-n-amyl-methane.

Empirical formula $C_{50}H_{54}N_4O_2$

Structural formula

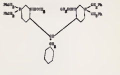
Crystalline form and color	White powder
Molecular weight	742.47
Melting point	201°C.
Yield	24%
Analyses	Found Calculated
Nitrogen	7.46% 7.55%
Solubilities	
Water	Insoluble
Alcohol	Very slightly soluble hot
Acetone	Slightly soluble hot
Acetic acid	Soluble hot
Dioxan	Soluble hot

21. Preparation of bis-(2-acetamino-4-dibenzylamino)-diphenyl-benzyl-methane.

Five grams (0.015 mole) of N,N-dibenzyl-N'-acetyl-m-phenylenediamine, 10 ml. (a large excess) of 50% phenylacetaldehyde in alcohol and 3.0 grams (0.0070 mole) of 28% sulfuric acid were dissolved in 40 ml. of 95% alcohol and heated in a sealed tube at 100°C. After two and one-half hours white crystals precipitated from the solution, which had become red during the heating. The heating was continued for two more hours and then the tube was allowed to cool and was opened. The crystals were separated from the mother liquor by filtration at the pump. The yield was 5.2 grams or 87% of the theoretical. The sample for analysis was purified by recrystallization from glacial acetic acid followed by extraction with alcohol and subsequent recrystallization from dilute dioxane. After drying the crystals in an Abderhalden apparatus, analysis for nitrogen showed 7.22% N. Calculated: 7.34% N. The melting point of the pure product was 240°C.

31. Bis-(3-acetamino-4-dibenzylamino)-diphenyl-benzyl-methane.

Empirical formula	$C_{52}H_{50}N_4O_2$
Structural formula	



Crystalline form and color	White powder	
Molecular weight	763.6	
Melting point	240°C.	
Yield	87%	
Analyses	Found	Calculated
Nitrogen	7.32%	7.34%
Solubilities		
Water	Insoluble	
Alcohol	Slightly soluble hot	
Acetone	Soluble hot	
Acetic acid	Soluble hot	
Dioxan	Soluble hot	

82. Preparation of bis-(2-acetamino-5-dibenzylamino)-diphenyl-omega-phenylethyl-methane.

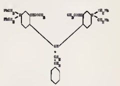
Six and six-tenths grams (0.02 mole) of N,N-dibenzyl-N'-acetyl-m-phenylenediamine, 4.0 grams (0.03 mole) of hydrocinnamaldehyde, and 1.0 gram (0.01 mole) of concentrated sulfuric acid were dissolved in 250 ml. of 95% alcohol and heated under reflux on the steam bath for four hours. There was no precipitate after this time so the flask was placed in the refrigerator and allowed to remain over a period of five days during which time white crystals precipitated very slowly from the solution. The crystals were separated from the mother liquor, which was red and showed strong green fluorescence, by filtration and were washed several times with alcohol. After drying the yield was 4.2 grams or 64% of the theory. The sample for analysis was crystallized from dilute dioxane and again from a mixture consisting of equal parts of benzene and heptane. It was dried in vacuo over sulfuric acid and nitrogen analysis showed 7.11% N. Calculated: 7.22% N. The pure substance showed a double melting point. If heated slowly on the Maquenne block or in a capillary tube in a bath, the compound melted sharply at 164°C. However, if crystals were dropped on the block as the temperature rose, the were applied at temperatures below 150°C. melted at 164°C. When the crystals were placed on the block at temperatures between 150°C. and 164°C. they melted first and then solidified

melting again at 184°C. Crystals applied at temperatures above 184°C. melted immediately and there was no subsequent solidification. This phenomenon is not caused by the loss of solvent of crystallization since the same melting points were observed no matter what solvent was used for recrystallization.

22. Bis-(3-acetamino-4-dibenzylamino)-diphenyl-omega-phenylethyl-methane.

Empirical formula $C_{53}H_{52}N_4O_2$

Structural formula



Crystalline form and color	White powder	
Molecular weight	776.4	
Melting point	104°C.	
Yield	84%	
Analysis	Found	Calculated
Nitrogen	7.11%	7.22%
Solubilities		
Water	Insoluble	
Alcohol	Slightly soluble hot	
Acetone	Slightly soluble hot	
Acetic acid	Soluble	
Dioxan	Soluble hot	

SUMMARY

I. N,N-Dibenzyl-m-phenylenediamine has been prepared in pure crystalline form and its use as an aldehyde reagent has been investigated and described. This test is believed to be of wider general usefulness than any previously devised for the detection of aldehydes.

II. The reactions which lead to the characteristic colors and fluorescences which appear in this test have been studied.

III. The following new Schiff bases from N,N-dibenzyl-m-phenylenediamine have been prepared and described:

(1) Benzylidene-m-dibenzylaminoaniline

(2) Salicylidene-m-dibenzylaminoaniline

(3) Anisylidene-m-dibenzylaminoaniline

(4) o-Methoxy-benzylidene-m-dibenzylaminoaniline

(5) p-Chloro-benzylidene-m-dibenzylaminoaniline

(6) Cinnamylidene-m-dibenzylaminoaniline

IV. The following new acyl derivatives of N,N-dibenzyl-m-phenylenediamine have been prepared and described:

(1) N,N-Dibenzyl-N',N'-diacetyl-m-phenylenediamine

(2) The m-dibenzylaminoanilide of maleic acid

V. The following new diphenylmethane derivative has been prepared from dibenzyl-m-phenylenediamine and formaldehyde:

(1) Bis-(2-amino-4-dibenzylamino)-diphenylmethane

VI. The following new diphenyl- and triphenylmethane derivatives have been prepared by condensing N,N-dibenzyl-N'-acetyl-m-phenylene-diamine with different aldehydes:

(1) 2,2'-Bis-acetamino-4,4'-bis-dibenzylamino-triphenylmethane

(2) 2,2'-Bis-acetamino-4,4'-bis-dibenzylamino-2''-chloro-triphenylmethane

(3) 2,2'-Bis-acetamino-4,4'-bis-dibenzylamino-4''-chloro-triphenylmethane

(4) 2,2'-Bis-acetamino-4,4'-bis-dibenzylamino-3'',4''-dimethoxy-triphenylmethane

(5) 2,2'-Bis-acetamino-4,4'-bis-dibenzylamino-3''-methoxy-triphenylmethane

(6) 2,2'-Bis-acetamino-4,4'-bis-dibenzylamino-4''-methoxy-triphenylmethane

(7) 2,2'-Bis-acetamino-4,4'-bis-dibenzylamino-3''-methyl-triphenylmethane

(8) 2,2'-Bis-acetamino-4,4'-bis-dibenzylamino-4''-methyl-triphenylmethane

(9) 2,2'-Bis-acetamino-4,4'-bis-dibenzylamino-3''-methoxy-4''-hydroxy-triphenylmethane

(10) 2,2'-Bis-acetamino-4,4'-bis-dibenzylamino-3'',4''-methylenedioxy-triphenylmethane

(11) 2,2'-Bis-acetamino-4,4'-bis-dibenzylamino-2''-nitro-triphenylmethane

(12) 2,2'-Bis-acetamino-4,4'-bis-dibenzylamino-3''-nitro-triphenylmethane

(13) 2,2'-Bis-acetamino-4,4'-bis-dibenzylamino-4"-nitro-triphenylmethane

(14) 2,2'-Bis-acetamino-4,4'-bis-dibenzylamino-2"-chloro-5"-nitro-triphenylmethane

(15) Bis-(2-acetamino-4-dibenzylamino)-diphenylmethane

(16) Bis-(2-acetamino-4-dibenzylamino)-diphenyl-methyl-methane

(17) Bis-(2-acetamino-4-dibenzylamino)-diphenyl-ethyl-methane

(18) Bis-(2-acetamino-4-dibenzylamino)-diphenyl-n-propyl-methane

(19) Bis-(2-acetamino-4-dibenzylamino)-diphenyl-n-amyl-methane

(20) Bis-(2-acetamino-4-dibenzylamino)-diphenyl-benzyl-methane

(21) Bis-(2-acetamino-4-dibenzylamino)-diphenyl-omega-phenylethyl-methane

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BIOGRAPHY

Frederick Gray Singleton was born on March 16, 1914 at Fort Meade, Florida. His undergraduate work was done at the University of Florida, from which institution he received the degree of Bachelor of Science, with Honors, in 1936.

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Committee Report

This dissertation was prepared under the direction of the Chairman of the candidate's Supervisory Committee, and has been approved by all members of the Committee. It was submitted to the Graduate Council and was approved as partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

Date August 24, 1940

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